# Reactivity Screening Made Easy

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## INTRODUCTION

During the past decade, large efforts were made by the U.S. chemical and petrochemical industries to implement and maintain effective process safety management (PSM) and responsible care programs. Despite these large investments, incidents continue to occur at an alarming frequency. Many executives of leading companies are trying to understand why.

A recent survey conducted by the U.S. Chemical and Safety Hazard Investigation Board (CSB) concluded that reactive chemicals present a significant safety problem for the chemical process industries (see Figure 1). Key root causes identified by the CSB survey included technical and management systems failures. This underscores the importance of the need to understand and manage chemical reaction hazards more effectively. We also believe that the "quality" of implementation, change management, and auditing of corporate PSM programs is the culprit.

We focus in this short paper on incidents caused by runaway reactions and provide guidance on how to improve the quality of managing chemical reactions hazards through a combination of screening and experimental tools.

The screening tool we offer is the culmination of more than a decade of active work in the area of reaction hazards focused on finding a simple method of determining potential reaction hazards with limited data. One can easily apply this simple hazard index to a wide variety of liquid-phase, gas-phase, and solid-phase reactions.

## THE CHEMISTRY IS KEY

"You cannot manage what you cannot measure" is a simple, yet effective concept practiced by many successful business professionals. The same principle applies to reaction chemistry. You will not be able to effectively manage chemical reaction hazards if you are unable to identify, measure, and control key reaction characteristics.

A key characteristic of a chemical reaction (such as a polymerization, decomposition, or combustion) deals with how much total energy potential is present that can be converted to mechanical work that can cause damage to property, life, and equipment.

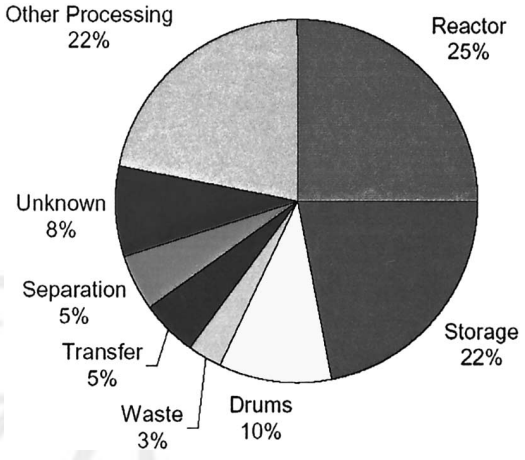


**Figure 1** Recent incident statistics involving reactive chemicals. Source: J. Murphy, CSB Public Hearing Staff Preliminary Conclusions, May 2002, Paterson, NJ. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com]

Other key reaction characteristics deal with the rate of release of such energy potential. An explosive works via a chemical reaction just like the commercial production chemical reaction of polymers with one major difference, "reaction rates." The reaction rates of an explosive can be several orders of magnitude faster than the reaction rates of typical commercial processes.

In order to effectively manage the hazard potential of chemical reactions, we need quantitative data on energy release rates, such as the following:

- Heat release rates ($dT/dt$);
- Mechanical energy release rates ($dP/dt$);
- Onset temperature of undesired reaction ($T_o$);
- Overall adiabatic heat of reaction;
- Shock sensitivity data;
- Chemical interaction data;
- Equipment scale-up data.

## AN EFFECTIVE AND SIMPLE HAZARD INDEX

Since 1995 we have been conducting experimental and theoretical work to develop reliable chemical reaction hazard prediction methods [1–8]. Our proposed

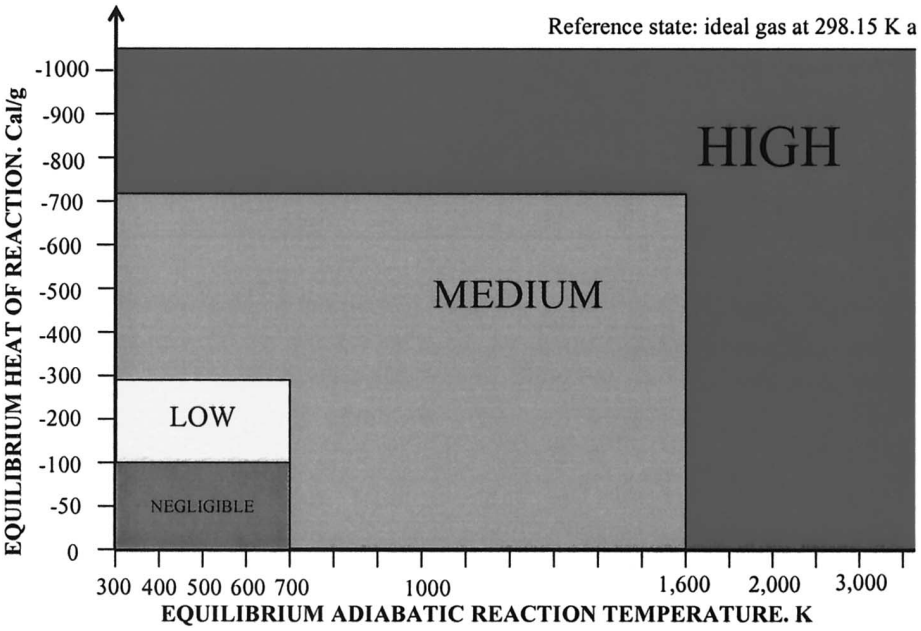


**Figure 2** The Melhem chemical reactivity hazard index/reactivity screening tool. Source: ioMosaic Corp. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com]

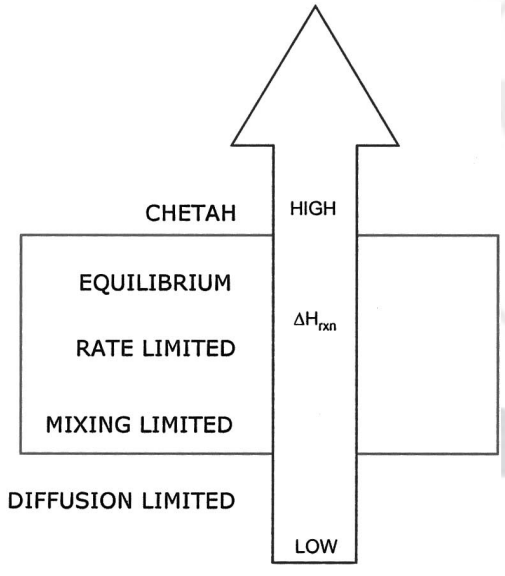


**Figure 3** Heat of reaction hazard scale. Source: IoMosaic Corp. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com]

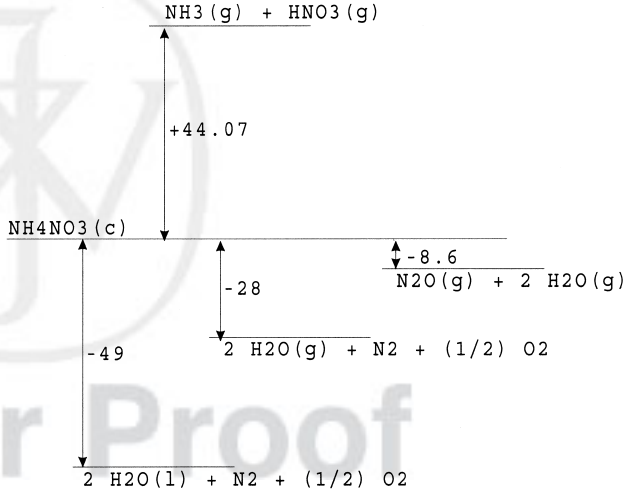


**Figure 4** Thermochemistry of ammonium nitrate (kcal/gmol AN). Source: ioMosaic Corp.

hazard index is based on the heat of reaction and the computed equilibrium[1] adiabatic reaction temperature (CART) as illustrated in Figure 2 and summarized below.

Fn1 F2

[1]Must be computed using a chemical equilibrium code at an ideal gas state of 1 bar and 298.15 K. For liquid reactions, latent heat effects are often small compared to the heat of reaction.

**D: Negligible or No Hazard Group**

This group has a heat of reaction no more negative than -100 cal/g (-0.42 kJ/g) and CART no more than 700 K.

**C: Low Hazard Group**

This group has a heat of reaction between -100 and -287 cal/g (-0.42 and -1.2 kJ/g) and CART no more than 700 K.

**B: Medium Hazard Group**

This group has a heat of reaction between -287 and -717 cal/g (-1.2 and -3.0 kJ/g) or CART greater than 700 and less than 1600 K.

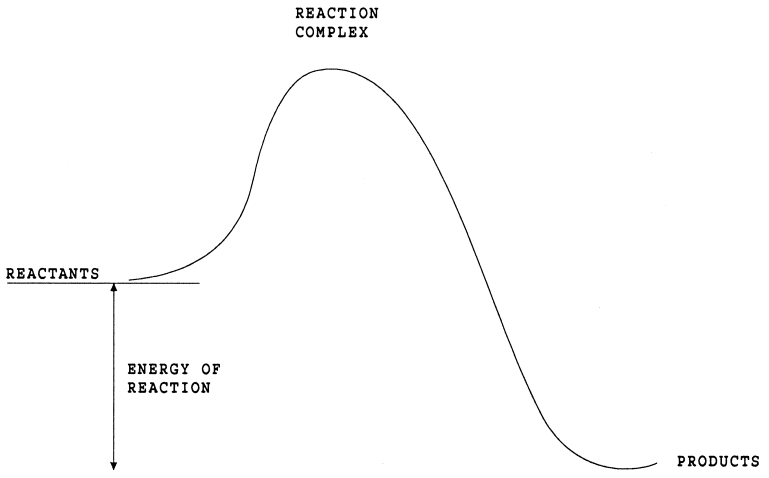


**Figure 5** Kinetics of a typical exothermic decomposition reaction. Source: ioMosaic Corp.

**A: High Hazard Group**

This group has a heat of reaction more negative than -717 cal/g (-3.0 kJ/g) or CART higher than 1600 K.

Reactions with a hazard index of D represent little or no reactivity hazard. Reactions with a hazard index of A represent a high hazard and a strong potential for being explosive. Such reactions often involve the use of a very active/explosive ingredient and should only be carried out using a diluent/solvent with a boiling point that is higher than the reaction onset temperature. A hazard index of B or C indicates a reaction system that may be energetic but that is not likely to result in an explosion hazard. These reactions can be conducted safely with proper safeguards that may include active temperature and pressure sensing and monitoring, relief devices, quench systems, etc.

This hazard index can be applied easily to a wide variety of reactions including liquid-phase reactions such as decompositions, polymerizations, reaction of two or more species, gas-phase reactions such as combustion reactions, deflagrations, and detonations, and reactions involving solids such as dust explosions.

The hazard index proposed here is supported by fundamental and experimental measurements. It has been tested and validated over the past decade using a variety of means including the following:

- Comparison of hazard prediction with compounds and reactions known to exhibit or known not to exhibit explosive behavior (Appendix A);
- Quantum mechanical validations using advanced computational tools (Appendix B);
- Blasting cap experimental studies (Appendix C); and
- Comparison of hazard prediction with compounds known to be flammable and/or detonate (Appendix D).

The proposed hazard index requires the estimation of heat of reaction and computed adiabatic flame temperature. The heat of reaction can easily be estimated using a variety of means including group contribution, heats of combustion, quantum chemistry, similarity, adiabatic calorimetry, reaction calorimetry, and isothermal calorimetry.

One should note that heats of reaction estimated by the ASTM CHETAH are very conservative since they are based on maximizing reaction enthalpy and not on an equilibrium estimate (see Figure 3). F3

The CART can easily be computed from chemical equilibrium programs such as the NIST CET93 program or SuperChems Expert. SuperChems Expert provides the ability to estimate CART for multiphase systems with nonideal effects caused by pressure, heats of solution, etc. The program also has built-in routines that enable the user to trace CART isotherms as a function of mixture composition.

**CASE STUDY: AMMONIUM NITRATE**

Ammonium nitrate (AN) manufacture begins with the synthesis of hydrogen gas, usually accomplished by reacting water with some reducing agent:

$$H_2O + C = H_2 + CO.$$

The hydrogen, at high pressure, is then reacted with nitrogen, which has been separated from air:

$$3\ H_2 + N_2 = 2\ NH_3.$$

The next step is the formation of nitric acid by oxidation of ammonia, using oxygen from the air:

$$NH_3 + 2\ O_2 = HNO_3 + H_2O.$$

The final step is the formation of ammonium nitrate by reaction between nitric acid and additional ammonia:

$$HNO_3 + NH_3 = NH_4NO_3.$$

**Table 1.** Blasting cap test data reported in Ref. [6].

| Run No. | Composition | D. Max. (cm) | Delta (D) | Volume (ml) | Delta V (ml) | D (g/cc) | Condition of Witness Tube | Delta $H_r$ (kJ/g), Gas Phase | CART K Reactants |
|---|---|---|---|---|---|---|---|---|---|
| 1A | Water | 4.48 | 0.25 | 206 | 2 | 1.00 | | | |
| 1 | Water | 4.52 | 0.29 | 210 | 4 | 1.00 | Small bulge at cap level | 0 | 298 |
| 2 | Dodecane | 4.50 | 0.27 | 210 | 5 | 0.73 | Ditto | −1.67 | 663 |
| 3 | Dodecane | 4.46 | 0.23 | 209 | 4 | 0.73 | Ditto | −1.67 | 663 |
| 4 | Toluene | 4.52 | 0.29 | 211 | 6 | 0.87 | Ditto | −2.16 | 859 |
| 5 | Toluene | 4.33 | 0.10 | 209 | 4 | 0.87 | Ditto | −2.16 | 859 |
| 6 | Mononitrotoluene | 4.53 | 0.30 | 208 | 3 | 1.16 | Ditto | −4.21 | 1573 |
| 7 | Mononitrotoluene | 4.47 | 0.24 | 208 | 3 | 1.16 | Ditto | −4.21 | 1573 |
| 8 | TNM-toluene 50/50 wt | 4.62 | 0.39 | 209 | 4 | 1.14 | Ditto | −4.44 | 1701 |
| 9 | Sodium chloride | 4.31 | 0.08 | 205 | 0 | 1.28 | Ditto | 0 | 298 |
| 12 | Anthracene | 4.68 | 0.45 | 210 | 5 | 0.72 | Ditto | −2.59 | 983 |
| 20 | Cumene hydroperoxide 80% | 4.52 | 0.29 | 209 | 4 | 1.02 | Ditto | −3.13 | 956 |
| 21 | Cumene hydroperoxide 80% | 4.57 | 0.34 | 209 | 4 | 1.02 | Ditto | −3.13 | 956 |
| 22 | Di *t*-butyl peroxide | 4.52 | 0.29 | 210 | 5 | 0.79 | Ditto | −2.72 | 847 |
| 23 | Di *t*-butyl peroxide | 4.50 | 0.27 | 208 | 3 | 0.79 | Ditto | −2.72 | 847 |
| 24 | Benzoyl peroxide | 4.30 | 0.07 | 206 | 1 | 0.71 | Ditto | −3.47 | 1016 |
| 25 | Benzoyl peroxide | 4.50 | 0.27 | 206 | 1 | 0.64 | Ditto | −3.47 | 1016 |
| 26 | $H_2O_2$ 40% + EtOH, balanced | 4.55 | 0.32 | 209 | 4 | 1.12 | Ditto | −3.39 | 1874 |
| 27 | $H_2O_2$ 40% + EtOH, balanced | 4.49 | 0.26 | 210 | 5 | 1.12 | Ditto | −3.39 | 1874 |
| 10 | Ammonium nitrate | 4.61 | 0.38 | 210 | 5 | 0.94 | Bulged and split | −2.37 | 1723 |
| 11 | Ammonium nitrate | 5.00 | 0.77 | 215 | 10 | 1.00 | Ditto | −2.37 | 1723 |
| 14 | Dinitrotoluene | 4.68 | 0.45 | 214 | 9 | 1.01 | Ditto | −5.76 | 1511 |
| 15 | Dinitrotoluene | 4.89 | 0.66 | 214 | 9 | 1.01 | Ditto | −5.76 | 1511 |
| 28 | $H_2O_2$ 50% + EtOH, balanced | 4.70 | 0.47 | 212 | 7 | 1.14 | Ditto | −4.14 | 2140 |
| 29 | $H_2O_2$ 50% + EtOH, balanced | 4.53 | 0.3 | 210 | 5 | 1.14 | Bulge at cap level | −4.14 | 2140 |
| 30 | AN + 2.5% dodecane | — | — | — | | 0.66 | Top of tube peeled open | −3.54 | 2168 |
| 31 | AN + 2.5% dodecane | — | — | — | | 0.66 | Top of tube peeled open | −3.54 | 2168 |
| 33 | Urea nitrate, S.M. | — | — | — | | 0.75 | Half of tube peeled open | −3.74 | 2468 |
| 34 | Urea nitrate, S.M. | — | — | 217 | 12 | 0.79 | Two splits | −3.74 | 2468 |
| 19 | TNM-toluene, balanced | — | — | — | | 1.22 | Tube shattered | −7.64 | 3082 |

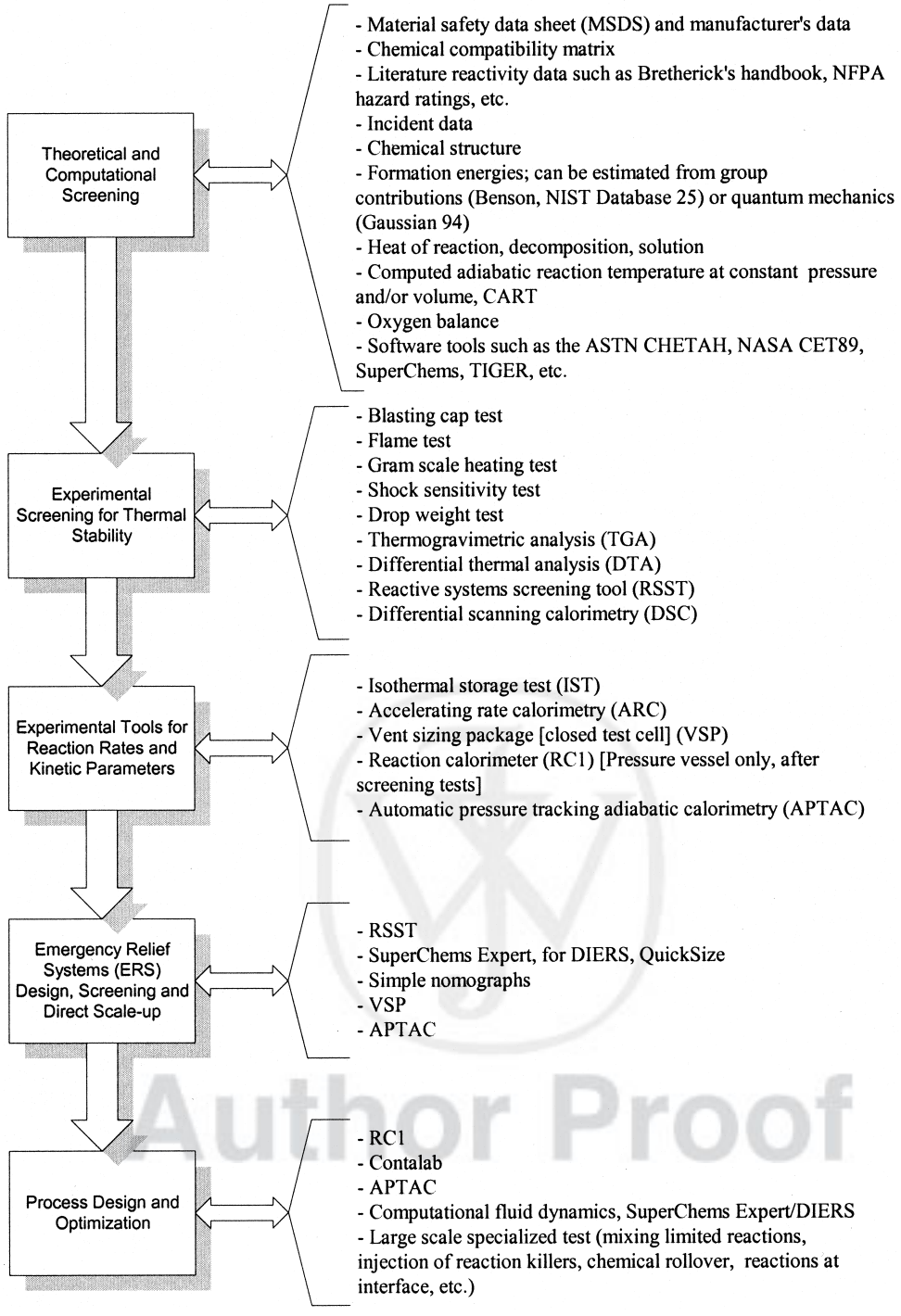


**Figure 6** Systematic evaluation of chemical reaction hazards. Source: Ref. [7].



Selected aspects of ammonium nitrate thermochemistry are summarized in Figure 4. These data illustrate the large effect that confinement can have upon the energetics of the decomposition. Confinement inhibits the endothermic vaporization and dissociation reaction and also favors the formation of liquid water during the decomposition reaction. The result is a large increase in the effective heat of reaction, leading to temperature rise and thermal runaway.

Figure 5 provides an illustration of the kinetics involved in typical exothermic decomposition reactions such as the decomposition of ammonium nitrate. Substances which can react to produce a new set of products while releasing energy are termed metastable. Many metastable substances, of which ammonium nitrate is an example, are quite long-lived in storage even though there is a strong driving force toward decomposition. The observed storage stability exists because of the energy barrier represented by the difference between the substance and its reaction complex.

In the case of ammonium nitrate the barrier is lowered by raising the temperature, adding chlorides, lowering the pH (increased acidity), and adding chromium and also by contaminants in general. Once the reaction complex energy level is reached a self-accelerating decomposition will occur, possibly culminating in nearly instantaneous decomposition (detonation) of the remaining unreacted material.

The CART and heat of reaction index of ammonium nitrate, fueled ammonium nitrate, and ammonium nitrate-urea place these two compositions in category A, high hazard. This is shown in Table 1 in Appendix C. T1

The CART value depends on the reaction mechanism and stoichiometry. It is also sensitive to isomers and the presence of diluents and/or other chemicals influencing the reaction, even if they are present in small quantities.

For example, the CART value of pure AN for the reaction producing water, oxygen, and nitrogen is 1723 K. The CART value for AN/2.5% dodecane is 2168 K, and the CART value for AN/urea mixture is 2684 K.

## SYSTEMATIC EVALUATION OF CHEMICAL REACTION HAZARDS

The chemical reaction hazard index proposed here is one of many tools that are available and that can be used to effectively manage chemical reactivity hazards. A summary of widely available computational and experimental tools is provided in Figure 6, taken from Ref. [7]. F6

## CONCLUSIONS

Reliable hazard prediction is valuable and the existing methods are not satisfactory. Work to date shows that a combination index of heat of reaction and CART provides a good screening indicator of reactivity hazard potential.

Reactivity screening is not intended to replace experimental data. Where possible, calorimetry data should be obtained using adiabatic and reaction calorimetry. The proposed hazard index can be used to help guide and focus the experimental calorimetry work and for rapid computational screening.

## APPENDIX A: SELECTED HAZARD INDEX PREDICTIONS VS. COMPOUNDS AND REACTIONS WITH KNOWN BEHAVIOR

A wide range of chemicals can be accurately screened using the heat of reaction and computed adiabatic reaction temperature. This small sample subset was taken from Ref. [4] to illustrate the use of our hazard index.

| | $\Delta H_r$ (kJ/g) | $\Delta H_r$ (cal/g) | CART (K) | Observed Behavior |
|---|---|---|---|---|
| CH and CHO compounds | | | | |
| Acetylene | −10.1 | −2438 | 2824 | Explosive |
| Ethylene | −4.2 | −1004 | 1253 | Nonexplosive |
| Furan | −3.6 | −860 | 995 | Nonexplosive |
| Acrylic acid | −2.2 | −526 | 789 | Nonexplosive |
| Oxalic acid | −1.2 | −287 | 416 | Nonexplosive |
| Organic N compounds | | | | |
| Glycerol dinitrate | −6.0 | −1434 | 2813 | Explosive |
| Mononitrotoluene | −4.2 | −1004 | 1104 | Nonexplosive |
| *p*-Nitroaniline | −3.4 | −813 | 1109 | Nonexplosive |
| *m*-Nitrobenzoic acid | −3.0 | −717 | 998 | Nonexplosive |
| REDOX compositions | | | | |
| Ammonium nitrate − urea | −4.1 | −980 | 2684 | Explosive |
| $H_2O_2$ 70% − ethanol | −3.8 | −908 | 2109 | Explosive |
| $HClO_4$ 70% − acetic acid | −3.5 | −837 | 2125 | Explosive |
| Organic peroxides | | | | |
| Acetyl peroxide | −0.8 | −191 | 956 | Explosive |
| Benzoyl peroxide | −0.7 | −167 | 972 | Explosive |
| Dicumyl peroxide | −0.7 | −167 | 925 | Nonexplosive |
| Di *t*-butyl peroxide | −0.7 | −167 | 847 | Explosive |
| Dilauroyl peroxide | −0.4 | −96 | 777 | Nonexplosive |
| Inorganic N compounds | | | | |
| Hydrozoic acid | −6.9 | −1649 | 3369 | Explosive |
| Mercury fulminate | −2.1 | −502 | 5300 | Explosive |
| Nitrogen trichloride | −1.9 | −454 | 1930 | Explosive |
| Lead azide | −1.6 | −382 | >4000 | Explosive |



## APPENDIX B: QUANTUM MECHANICAL VALIDATION

While at Arthur D. Little, Inc., Novikov, Weber, Shanley, and Melhem pursued quantum mechanical estimates of hazard predictions using Cerius 2, a software package developed by Accelerys.

Figure 7 illustrates the use of quantum mechanical software to aid in the estimation of hazard potential. F7

The impacts of energy differences between frontier orbitals that involve the weakest bond in the molecule are compared to the energy that is released when that particular bond breaks.

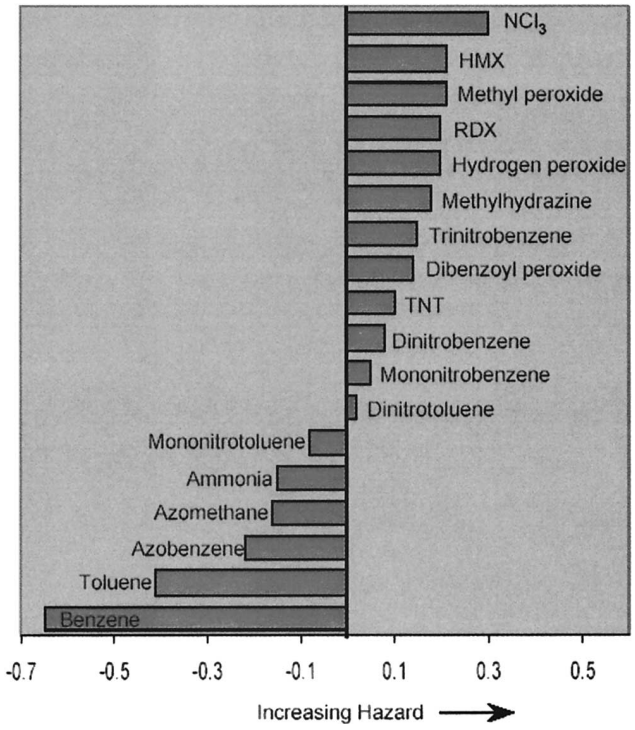


**Figure 7** Quantum mechanical estimates of hazard potential. Source: Arthur D. Little, Inc./TIAX LLC. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com]

**Figure 8** The Arthur D. Little blasting cap test. Source: Ref. [6]. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com]

The correlation proposed by Arthur D. Little, Inc., has been found to apply to a wide range of energetic molecules and free radical initiators.

This method can be applied to molecules whose thermochemistry is not available (or not measurable).

#### APPENDIX C: BLASTING CAP VERIFICATION OF THE MELHEM/SHANLEY HAZARD INDEX

We have also conducted a series of blasting cap tests to establish the validity of our proposed hazard index. These validation studies were conducted using the blasting cap test method established by Arthur D. Little (see [6]).

The Arthur D. Little blasting cap test (Figure 8) provides a means for assessing the sensitivity of a new composition to relatively intense impact and can produce valid comparisons between new compositions and better known materials whose hazardous properties are already established.

The blasting cap test data reported by Melhem in Ref. [6] is summarized in Table 1.

#### APPENDIX D: COMPARISON OF HAZARD INDEX WITH MATERIALS KNOWN TO BE FLAMMABLE AND/OR DETONATE

The hazard index proposed here can also be applied to combustion reactions and presents a very useful method for establishing flammability limits, detonation limits, and the flash point for mixtures.

In 1997, Melhem [5] showed that flammability and detonation limits for mixtures could be established using the CART method by direct minimization of the free energy. Since the flash point of a mixture corresponds to the temperature at which the bubble point of the mixture produces a flammable mixture at the lower flammability limit, it would be straightforward to estimate such a limit at a fixed CART point. Sharkey et al. [9] conducted an analysis on the flash point of ethanol–water using the CART method and showed excellent agreement with experimental data (see Figures 9–11). F8

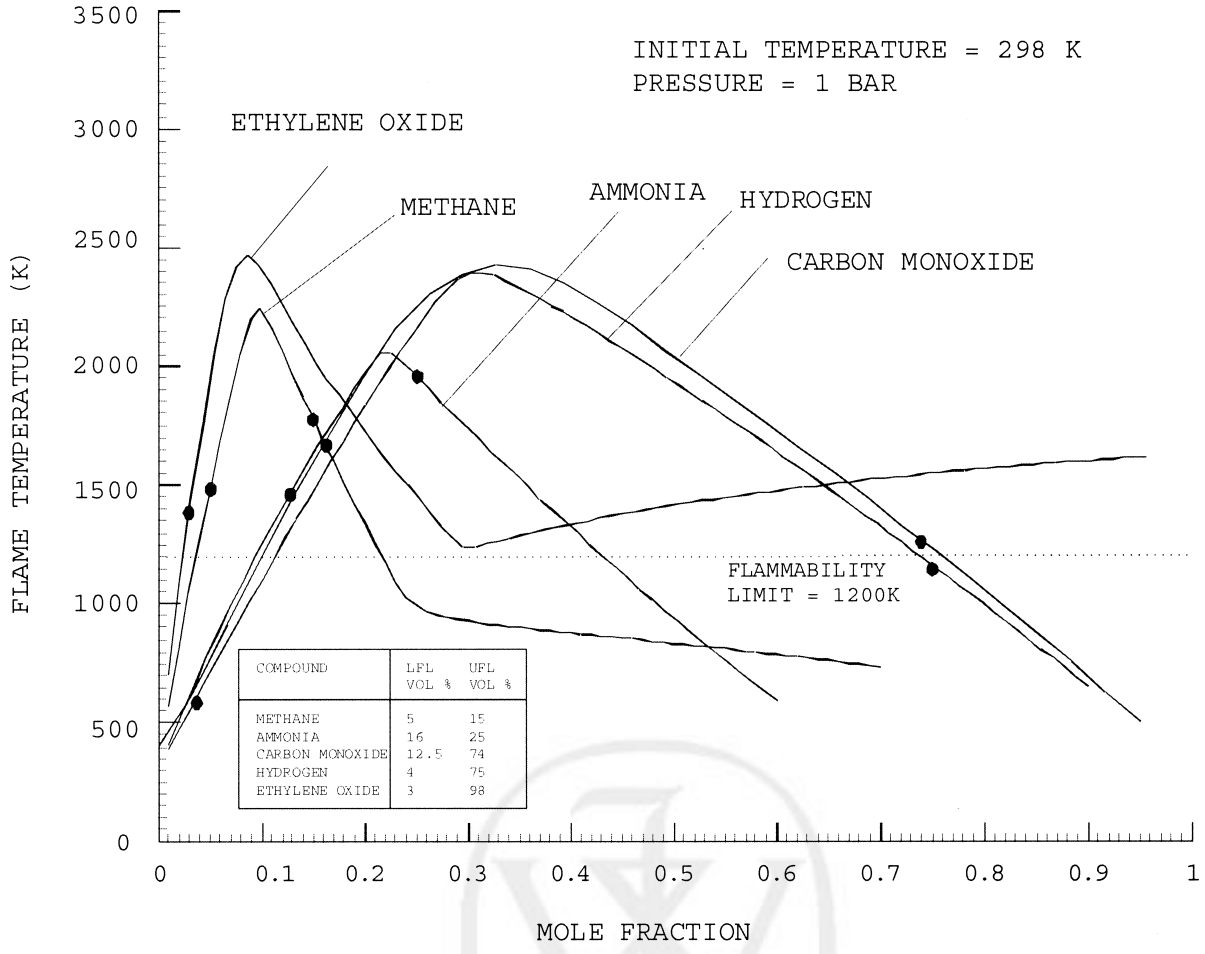


**Figure 9** A comparison of the CART hazard index with flammability limits at 1200 K. Source: ioMosaic Corp.

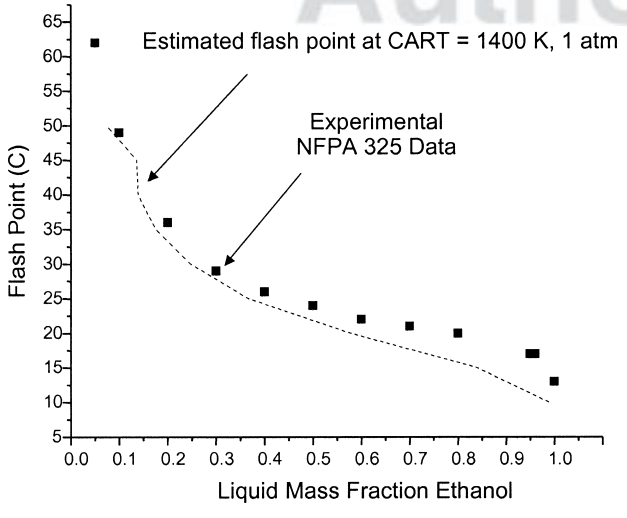


**Figure 10** The use of CART for the estimation of mixture flash points. Source: Ref. [9].

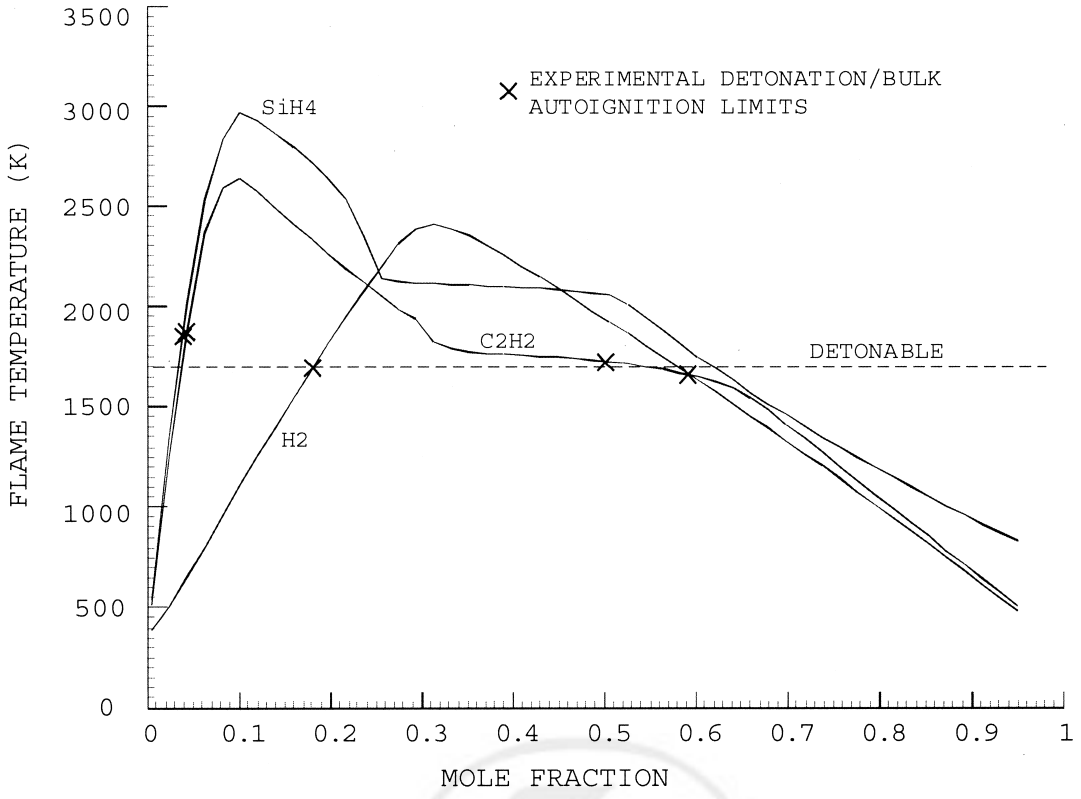


**Figure 11** Hazard index comparisons with detonation limits. Source: ioMosaic Corp.

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